

PROCESS AND APPARATUS FOR THE CONTINUOUS PRETREATMENT OF METAL ROIL STRIP PARTICULARLY STRIP INTENDED FOR THE MANUFACTURE OF LITHOGRAPHI C PLANOGRAPHIC PRINTING PLATES

Publication number: GB1374787 (A)

Publication date: 1974-11-20

Inventor(s):

Applicant(s): KALLE AG

Classification:

- international: B08B3/12; B41N3/04; C25D11/04; C25D17/00; B08B3/12; B41N3/00; C25D11/04; C25D17/00; (IPC1-7): C23B9/00; C23B3/00

- European: B08B3/12B; B41N3/04; C25D11/04; C25D17/00

Application number: GB19710060415 19711229

Priority number(s): DE19702064354 19701230

Also published as:

NL7117471 (A)

DE2064354 (A1)

AT320681 (B)

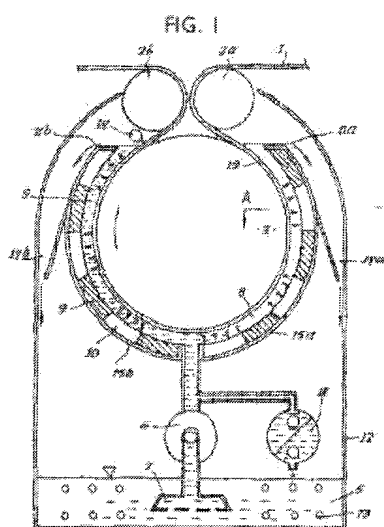
BE777422 (A1)

FR2121125 (A5)

more >>

Abstract of GB 1374787 (A)

1374787 Electro-chemical roughening, anodizing moving strip KALLE AG 29 Dec 1971 [30 Dec 1970] 60415/71 Heading C7B A metal (e.g. Al or Al alloy) foil strip, for manufacturing lithographic planographic printing plates, is continuously pretreated by mechanical e.g. sand-blasting or brushing, chemical or electrochemical roughening in acid, alkaline or neutral solution, e.g. an HCl electrolyte containing Hg ions, and/or anodic oxidation to produce thereon an (hydrated) oxide layer, e.g. using as electrolyte a solution of nitric, sulphuric, chromic, oxalic, acetic, malonic or lactic acid with A.C. or D.C., wherein, to avoid or remove sludge deposits on the metal surfaces during and/or after the pretreatment stages, ultrasonics of a frequency of at least 10 Kc/s act on the surfaces whilst the strip and a liquid are moved relative to one another at a speed of 0.5 - 50m/sec.; Preferably the strip 1 moves uniformly via rollers 2a, b through a slit-like channel 8, formed by driven insulated drum 3 and alternate electrodes 9 and ultrasonic vibrators 10, and through which appropriate electrolyte 5 is forced from storage vessel 12 via filter 7 by pump 6 to flow back via overflows 11 and conduits 17. The strip may be treated electrolytically and with ultrasonics on the same or opposite surfaces. The electrodes themselves may be constructed as ultrasonic vibrators. Individual electrodes and vibrators may be wholly or partly screened. An electrolyte for roughening Al is specified containing 1% HNO₃ and 0.25% Al (NO₃)₃.



Data supplied from the esp@cenet database — Worldwide

1 374 787

(21) Application No. 60415/71 (22) Filed 29 Dec. 1971

(19)

(31) Convention Application No. 2 064 354

(32) Filed 30 Dec. 1970 in

(33) Germany (DT)

(44) Complete Specification published 20 Nov. 1974

(51) International Classification C23B 9/00 3/00

(52) Index at acceptance

C7B 13 17 2F 3B A1E A2C10 A2C12 A2C2 A2C5 A2F



(54) PROCESS AND APPARATUS FOR THE CONTINUOUS PRETREATMENT
OF METAL FOIL STRIP, PARTICULARLY STRIP INTENDED FOR THE
MANUFACTURE OF LITHOGRAPHIC PLANOGRAPHIC PRINTING PLATES

SPECIFICATION NO 1374787

By a direction given under Section 17 (1) of the Patents Act 1949 this application proceeded in the name of HOECHST AKTIENGESELLSCHAFT, a Body Corporate organised according to the laws of Germany, of 6230 Frankfurt/Main 80, Germany.

THE PATENT OFFICE

R 78417/8

apparatus for the continuous pretreatment of metal foil strip, particularly strip intended for the manufacture of lithographic planographic printing plates.

15 It is known that for use as supports in lithographic planographic printing plates certain metal foils must in general be subjected to an intensive pretreatment in order to render them suitable to support the print
20 image which is to be applied. Thus the metal foil must almost always be subjected to a cleaning process, above all in order to remove the remnants of grease or oil originating from the rolling process, and the surface
25 intended to receive the print image must subsequently be roughened. The foil is cleaned by washing, for example with organic solvents, or by a chemical or electrochemical treatment, and mechanical or again chemical
30 or electrochemical, processes are used for the roughening. Suitable roughening processes are, for example, sand-blasting or brushing of the metal surface. For chemical or electrochemical roughening, acid, alkaline
35 or neutral electrolytes are in general use, and in the case of electrochemical roughening, hydrochloric acid, which can optionally also contain additives, such as mercury ions and the like, is preferred. Direct
40 current or alternating current, the latter being frequently preferred, can be used for the electrochemical roughening; superimposed currents can also be of advantage.

45 The cleaned and roughened metal foils are usually subsequently subjected to an anodic oxidation in order to produce on them a thin layer of oxide or hydrated oxide

and conditions and electrical parameters, a variable surface character generally results, showing, on microscopic examination, a crater-like to irregular cleft appearance, with the individual raised areas in each case additionally containing minute pore-like orifices, which are presumably principally responsible for the anchoring of the print
65 image. It is therefore of great importance that these pore-like orifices should be obtained in a condition where they are as free as possible from contamination.

It is known that both during the roughening and during the subsequent anodic oxidation, sludge-like deposits of reaction products form between the metal and the treatment liquid, which fill the recesses in the metal surface and in particular cover or clog the above-mentioned pores. Additionally, the layer of sludge formed exerts an insulating effect during the electrochemical treatments, slowing down the roughening or oxidation process. It has been found that the sludge-like deposits cannot be completely removed by a simple washing process, and a series of auxiliary measures has therefore already been employed.

The removal of the layer of sludge by
85 mechanical means, such as brushing or rubbing off with a sponge, is difficult and furthermore leads to a non-uniform surface. The damage of the metal surface, which is sensitive to mechanical stresses, such damage
90 being unavoidable in the course of the above process, and the non-uniform cleaning of the metal surface, result in an increase in the proportion of scrap, above all in the

(21) Application No. 60415/71 (22) Filed 29 Dec. 1971

(19)

(31) Convention Application No. 2 064 354

(32) Filed 30 Dec. 1970 in

(33) Germany (DT)

(44) Complete Specification published 20 Nov. 1974

(51) International Classification C23B 9/00 3/00

(52) Index at acceptance

C7B 13 17 2F 3B A1E A2C10 A2C12 A2C2 A2C5 A2F



(54) PROCESS AND APPARATUS FOR THE CONTINUOUS PRETREATMENT
OF METAL FOIL STRIP, PARTICULARLY STRIP INTENDED FOR THE
MANUFACTURE OF LITHOGRAPHIC PLANOGRAPHIC PRINTING PLATES

(71) We, KALLE AKTIENGESELLSCHAFT, a body corporate organised according to the laws of Germany, of 190—196 Rheingastrasse, Wiesbaden-Biebrich, Germany, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention concerns a process and apparatus for the continuous pretreatment of metal foil strip, particularly strip intended for the manufacture of lithographic planographic printing plates.

It is known that for use as supports in lithographic planographic printing plates certain metal foils must in general be subjected to an intensive pretreatment in order to render them suitable to support the print image which is to be applied. Thus the metal foil must almost always be subjected to a cleaning process, above all in order to remove the remnants of grease or oil originating from the rolling process, and the surface intended to receive the print image must subsequently be roughened. The foil is cleaned by washing, for example with organic solvents, or by a chemical or electrochemical treatment, and mechanical or again chemical or electrochemical, processes are used for the roughening. Suitable roughening processes are, for example, sand-blasting or brushing of the metal surface. For chemical or electrochemical roughening, acid, alkaline or neutral electrolytes are in general use, and in the case of electrochemical roughening, hydrochloric acid, which can optionally also contain additives, such as mercury ions and the like, is preferred. Direct current or alternating current, the latter being frequently preferred, can be used for the electrochemical roughening; superimposed currents can also be of advantage.

The cleaned and roughened metal foils are usually subsequently subjected to an anodic oxidation in order to produce on them a thin layer of oxide or hydrated oxide

which promotes good adhesion to the print image subsequently to be applied. Suitable electrolytes generally used in the anodic oxidation are solutions of inorganic acids, for example nitric acid, sulphuric acid or chromic acid, or organic acids, such as oxalic acid, acetic acid, malonic acid or lactic acid. Depending on the nature and concentration of the electrolytes used, and also depending on the preselected temperature conditions and electrical parameters, a variable surface character generally results, showing, on microscopic examination, a crater-like to irregular cleft appearance, with the individual raised areas in each case additionally containing minute pore-like orifices, which are presumably principally responsible for the anchoring of the print image. It is therefore of great importance that these pore-like orifices should be obtained in a condition where they are as free as possible from contamination.

It is known that both during the roughening and during the subsequent anodic oxidation, sludge-like deposits of reaction products form between the metal and the treatment liquid, which fill the recesses in the metal surface and in particular cover or clog the above-mentioned pores. Additionally, the layer of sludge formed exerts an insulating effect during the electrochemical treatments, slowing down the roughening or oxidation process. It has been found that the sludge-like deposits cannot be completely removed by a simple washing process, and a series of auxiliary measures has therefore already been employed.

The removal of the layer of sludge by mechanical means, such as brushing or rubbing off with a sponge, is difficult and furthermore leads to a non-uniform surface. The damage of the metal surface, which is sensitive to mechanical stresses, such damage being unavoidable in the course of the above process, and the non-uniform cleaning of the metal surface, result in an increase in the proportion of scrap, above all in the

50

55

60

65

70

75

80

85

90

manufacture of presensitised printing plates.

The published documents of German Patent Application K 9115/48a describe a process for the anodic oxidation of metals in which, during the anodic oxidation and, if appropriate, during all pretreatments or after-treatments, the treatment liquid is caused to undergo vibrations of high frequency by means of an ultrasonic generator. Though this process certainly results in extensive removal of the layers of sludge from the metal surface, it nevertheless does not represent a solution of the problem which is satisfactory in all respects. The reason for this is above all that during the treatment with ultrasonics the metal foils are excited into undergoing natural vibrations, which result in nodal lines and hence in linear vibration patterns indicated by deposits of the sludge which have remained adhering.

The present invention provides a process for the continuous pretreatment of a metal foil strip which in particular may be intended for the manufacture of lithographic planographic printing plates and which consists preferably of aluminium or an aluminium alloy, by mechanical, chemical or electrochemical roughening and/or anodic oxidation wherein, to avoid or remove sludge-like deposits on the metal surfaces during and/or after the pretreatment stages ultrasonics of a frequency of at least 10 kilo cycles per second are allowed to act on the surfaces while in contact with a liquid, during which action the metal foil strip and the liquid which contacts the latter are moved relative to one another at a speed of 0.5—50 m/second.

The liquid may be a liquid that is employed for the roughening or oxidation, or it may be a further liquid, as for example when the treatment is mechanical. In either case, the ultrasonic "treatment" in the liquid may be simultaneous with or subsequent to the roughening or oxidation.

It has been found that vibration patterns are no longer produced on the metal foil strip when during the action of ultrasonics the metal foil strip and the treatment liquid are moved relative to one another at the said speed.

A preferred range of relative speeds between the treatment liquid and the metal foil is 5—15 m/second. Particularly good results are achieved when the treatment liquid is passed through a relatively narrow slit along the uniformly moving metal foil strip. This slit can have an orifice of a width of 0.1—50 mm, preferably 1—20 mm. This not only results in a comparatively high relative speed, but also, through maintaining largely turbulent flow of liquid, additionally assists detachment of all sludge particles from the foil surface. The fre-

quency of the ultrasonics used must not be too low. Excellent results are achieved, in particular, in the frequency range of 20—40 kilocycles per second.

A process for the anodic polishing of metals is already known from German Patent Specification No. 945,423, in which the bath liquid is treated with ultrasonics of relatively low frequency, of 1,000 to 3,000 cycles per second, and the articles to be polished are successively or simultaneously moved through a large bath. This process is however not, or not sufficiently suitable for the removal of deposits, the problem to which the present invention is directed, because of the low frequency of the ultrasonics used and the low speed of movement of the articles in the treatment bath.

Additionally, German Published Specification No. 1,108,536 has already described a process for forming ultra-hard surfaces on aluminium by anodic oxidation, in which a controlled relative movement of the order of magnitude of more than 10 cm/minute per centimetre of anode surface is maintained between the electrolyte and the anode. In this process, however, no ultrasonic treatment is used.

The use of the process of the present invention results in a perfectly sludge-free, extremely uniformly roughened and anodised metal foil, which as a result of the anodic oxidation and of the complete baring of the surface microstructures required for anchoring, especially of the pole-like recesses, provides, after application of the print image, an offset printing plate which is extremely suitable for long printing runs.

However, the technical advance inherent in the process of the invention is not limited to the exhaustive removal of the sludge layers or the prevention of their formation, but also includes an acceleration of the electrochemical processes themselves. This is because the undesired sludge layers exert an electrical insulating effect, which greatly impedes the passage of the current. As a result of the complete removal of the sludge layers, the electrochemical processes on the metal surface and in the pore-like recesses are accelerated without increasing the electrical parameters, the metal ions produced by dissolving parts of the metal from the surface are rapidly flushed away from the vicinity of the surface, and sludge-like deposition of metal compounds is prevented, and this in turn intensifies the action of ultrasonics on the metal surface. The action of ultrasonics is principally to produce small cavitation bubbles, which cause a pulsating flow of electrolyte even in the vicinity of the surface and above all in the pore-like recesses of the metal surface or metal oxide layer, which recesses increase in size from the outside inwards. This pulsating flow of electro-

lyte is thus principally responsible for the removal of sludge particles from the pores and additionally assists the flushing effect caused by the comparatively high relative motion between the metal foil strip and the electrolyte solution in the surface region.

Current densities within a wide range, say between 5 and 500 amp/dm², can be used for the electrochemical roughening and anodic oxidation, and the current density to be used in each individual case depends on the remaining process parameters, such as the type of electrolyte and the concentration of electrolyte, the temperature and the desired surface character of the metal foil. The flow of the electrolyte through a narrow slit-shaped channel between the metal foil strip and the electrodes, which is brought about in accordance with the preferred embodiment of the process according to the invention, reduces the electrical resistance of the electrolyte and hence provides favourable conditions for the use of high current densities. The high relative speed between the metal foil strip and the electrolyte which prevails in the narrow channel additionally results in rapid removal of the heat generated, that is to say in the temperature remaining very largely constant during the process.

The process of the invention can for example be carried out by treating the metal foil strip simultaneously electrolytically and with ultrasonics in the course of the electrochemical roughening or anodic oxidation, this method resulting in particularly advantageous space utilisation of the treatment zone. In another variant, the electrolytic process and the action of ultrasonics alternate, preferably repeatedly, during the particular treatment stage. In this case, the sludge formed on the metal surface during one electrolytic process is completely removed during the subsequent treatment with ultrasonics, assisted by the relative movement between the metal foil strip and the electrolyte, so that the next electrolytic process can again exert an optimum effect on a clean metal surface or metal oxide surface. Within the field of electrolytic roughening, an extremely uniform surface etching is achieved with each variant of the process of the invention, and the danger of hole formation in the metal foil is completely avoided. As a result of the great acceleration of the electrolytic process, the roughening time, which in the conventional bath method is of the order of magnitude of a few minutes, can be reduced to as little as a few seconds if the process parameters are particularly favourably selected. This renders it possible to employ high speed treatment installations which can, additionally, be kept compact.

All variants of the process of the inven-

tion also have a similar favourable effect in the field of anodic oxidation. This is because the roughened surface is oxidised inwards from the outside, in the course of which the pore-like recesses, which have already been repeatedly referred to, allow the current to be transported to the metal underneath. The active exchange of material which results from the use in conjunction of electrolyte, ultrasonic action and relative movement between the metal foil strip and the electrolyte, and the fact, resulting therefrom, that the pores are kept free, increase the speed of anodisation and uniformity of anodisation considerably.

Further variations of the process of the invention depend on whether the particular electrolytic process and the action of ultrasonics are applied to the same surface or to opposite surfaces of a metal foil strip. This is because it has been found, surprisingly, that even on treatment with ultrasonics of the rear face of the electrochemically treated metal foil strip, with assistance from the relative motion between foil and electrolyte, perfect and complete removal of the sludge layer is ensured.

The invention also provides an apparatus for carrying out the process of the invention, which apparatus includes a housing with a slit-like fluid-tight channel therethrough and guide rollers for the metal foil strip, at least one of which rollers can be driven, arranged to guide the strip into and out of the said channel, electrodes for electrolysis and ultrasonic vibrators being arranged on the wall or walls of the channel adjacent the surface thereof and supply means being provided to maintain liquid within the channel, the arrangement being such that in the channel the metal foil strip and the treatment liquid can be moved relative to one another at a speed of 0.5—50 m/second. In one particular embodiment, the electrodes and the ultrasonic vibrators face the same metal foil surface in a repeatedly alternating sequence. In another embodiment, which is particularly advantageous when using direct current, that is to say especially during anodic oxidation, the electrodes are themselves constructed as ultrasonic vibrators. Since, in this case, parts of the apparatus are exposed both to electrochemical cavitation attacks and to cavitation attacks due to the action of ultrasonics, it is advantageous to use titanium as the constructional material. These embodiments of the apparatus of the invention are intended for use in one or other of the specific processes described above.

Since it is desirable to vary the duration of the action of ultrasonics from case to case, as a function of the current density and of the nature and concentration of the electrolyte, and to adapt them to the par-

ticular electrolytic treatment stage, the apparatus of the invention is preferably provided with screens by means of which the ultrasonic vibrators can be partially or wholly screened off so that their effective number and width can be varied. A similar arrangement may be provided for the electrodes, the number and effective width of which can also be varied by insulating screens.

The invention is illustrated by way of example in the accompanying drawings, in which:

Fig. 1 is a sectional elevation of one embodiment of the apparatus according to the invention;

Fig. 2 is a part of a cross-section on the line AB of Fig. 1;

Fig. 3 is a similar view to Fig. 1 of a further embodiment of the apparatus according to the invention; and

Fig. 4 is part of a cross-section on the line CD of Fig. 3.

Referring to the drawings, in Figs. 1 and 2, a metal foil strip 1, which enters the apparatus via a guide roller 2a, passes around a driven drum 3 over an arc of about 340° angle and then leaves via a guide roller 2b. The drum 3 is partly surrounded, at an approximately equal spacing, by alternate electrodes 9 and ultrasonic vibrators 10, all of which rest on a wall 15a, b which provides an insulation against tracking currents and a seal against liquid, thereby producing a slit-like treatment channel 8 which is laterally delimited by walls 16a, b. The electrodes 9 can be fed with direct current or alternating current, whereby the treatment device can be adapted to a particular pretreatment method. The individual electrodes 9 and the ultrasonic vibrators 10 can be wholly or partly covered by screens 20a, b, whereby they can be adjusted to the width of the metal foil strip 1 and the intensity of the electrolytic treatment and treatment with ultrasonics can be varied by completely covering one or other electrode or one or other ultrasonic vibrator. The drum 3 is insulated from the metal foil strip 1 and electrolyte 5 by an electrical insulating layer 19, which consists of an electrolyte-resistant and cavitation-resistant lacquer or of an adhesive film possessing these properties. This insulating layer 19, which is necessary when using the central conductor process, in which the electrodes 9 are insulated from all sides in such a way that only their active surface, facing the metal foil surface which is to be treated, is available for the passage of current, is omitted when using the contact process.

The electrolyte 5 appropriate to the particular pre-treatment stage is forced from a storage vessel 12 by a feed pump 6 via a filter 7 into the treatment channel 8, and

after flowing through the latter it flows back into the storage vessel 12 via overflows 11a, b and conduits 17a, b. A cooling system 13 which serves to control the temperature of the electrolyte 5 is provided in the storage vessel 12, and the electrolyte is topped up, when necessary, by adding material from a regeneration system 14.

After leaving the treatment channel 8 the metal foil strip 1 is blown dry by means of an air brush 18.

The apparatus of Figs. 1 and 2 can be modified in such a way that the electrodes 9 are themselves constructed as ultrasonic vibrators 10.

The apparatus of Figs. 3 and 4 corresponds to the device described above in respect of many of the constructional components. However, the metal foil strip 1 is passed over two drums 3a, b, of which one drum, or both synchronously, is or are equipped with a drive. The most important difference, however, is that the electrodes 9a, b on the one hand and the ultrasonic vibrators 10a, b on the other, face opposite surfaces of the metal foil strip 1 which is freely guided between the two drums 3a, b. This arrangement provides the possibility of a simultaneous electrolytic treatment and treatment with ultrasonics of the metal foil strip. The slit-shaped treatment channel 8 is in this case subdivided into a part 4 which is on the electrode side and a part 4¹ which faces the ultrasonic vibrators.

The principle of construction of the device according to Figs. 3 and 4 is also applicable to a horizontally extended installation, in which case it is advisable to locate the electrodes 9 above, and the ultrasonic vibrators 10 below, the metal foil strip 1 which is carried horizontally. The pressure head above the component treatment channels 4, 4¹ can in this case be regulated by, for example, an adjustable level vessel above the electrodes.

The invention is illustrated by the following Examples:

Example 1

An 0.3 mm thick aluminium foil strip of 150 mm width, which had beforehand been degreased in an alkali bath, was passed at a speed of 20 m/minute through the apparatus of Fig. 1. The apparatus was fed with 1% strength nitric acid which additionally contained 0.25% by weight of aluminium nitrate. This electrolyte, which was kept at a temperature of 15°C by cooling, was pumped through the treatment channel 8 at such a speed that the speed relative to the foil strip was about 7 m/second. The electrodes 9 fed with alternating current (50 cycles) were at a distance of about 5 mm from the foil strip; the voltage was so chosen that a current density of about 80 amp/dm²

resulted. Ultrasonics of about 20 kilocycles were generated by the ultrasonic vibrations 10. The foil strip which left the device after a dwell time of about 11 seconds was rinsed with water and dried. The foil strip 5 was found to be very uniformly roughened on the treatment side and the treated surface was completely free from sludge deposits, including sludge vibration patterns.

Example 2

The foil strip roughened according to Example 1 was anodised in 12% strength sulphuric acid in the apparatus of Fig. 1, 15 using direct current of such a voltage as to result in a current density of about 120 amp/dm². The remaining conditions were as indicated in Example 1.

An extremely uniformly anodised foil 20 strip was obtained, which was completely free from sludge deposits and sludge vibration patterns. The foil strip was outstandingly suitable for coating with light-sensitive layers and producing offset printing plates 25 for long printing runs.

Comparison Experiment:

Pieces of about 25 cm length were cut from the foil strip roughened according to 30 Example 1 and anodised in a customary electrolysis vessel. In doing so, analogous to Example 2, 12% strength sulphuric acid at 15°C was used as the electrolyte, and direct current of such a voltage was used at 35 an electrode distance of about 10 cm as to result in a current density of about 17 amp/dm². At the same time, the foil surfaces were treated with ultrasonics of about 40 20 kilocycles. After a period of treatment of 5 minutes, the cut pieces were removed from the electrolysis vessel, rinsed and dried. Whilst their anodisation was acceptable, their surface was covered with distinctly visible sludge lines, so that they were un- 45 suitable for the manufacture of quality printing plates.

WHAT WE CLAIM IS:—

1. A process for the continuous pretreat- 50 ment of a metal foil strip, which in particular may be intended for the manufacture of lithographic planographic printing plates, by mechanical, chemical or electrochemical roughening and/or anodic oxidation where- 55 in, to avoid or remove sludge-like deposits on the metal surfaces during and/or after the pretreatment stages ultrasonics of a frequency of at least 10 kilocycles per second are allowed to act on the surfaces while in contact with a liquid, during which action 60 the metal foil strip and the liquid which contacts the latter are moved relative to one another at a speed of 0.5—50 m/second.

2. A process as claimed in claim 1, 65 wherein the strip is made of aluminium or an aluminium alloy.

3. A process as claimed in claim 1 or 2, wherein the metal foil strip and the liquid which comes into contact therewith are moved at a speed of 5—15 m/second rela- 70 tive to one another.

4. A process as claimed in any one of claims 1 to 3, wherein the liquid is guided through a narrow slit along a metal foil strip uniformly moving through said slit.

5. A process as claimed in any one of claims 1 to 4, wherein ultrasonics of a fre- 75 quency of 10—40 kilocycles per second is employed.

6. A process as claimed in any one of claims 1 to 5, wherein during the electro- 80 chemical roughening and/or the anodic oxidation the metal foil strip is repeatedly treated alternately electrolytically and with ultrasonics.

7. A process as claimed in any one of claims 1 to 5, wherein during the electro- 85 chemical roughening and/or anodic oxidation, the metal foil strip is simultaneously treated electrolytically and with ultrasonics.

8. A process as claimed in claim 6 or 7, wherein the metal foil strip is treated 90 electrolytically and with ultrasonics on the same surface.

9. A process as claimed in claim 6 or 7, wherein the metal foil strip is treated 95 electrolytically and with ultrasonics on opposite surfaces.

10. A process as claimed in claim 1, substantially as described in either of Ex- 100 amples 1 and 2 herein.

11. A metal foil strip, when treated by the process claimed in any one of claims 1 to 10.

12. An apparatus for carrying out the process claimed in claim 1, which apparatus 105 includes a housing with a slit-like fluid-tight channel therethrough and guide rollers for the metal foil strip, at least one of which rollers can be driven, arranged to guide the strip into and out of the said channel, elec- 110 trodes for electrolysis and ultrasonic vibrators being arranged on the wall or walls of the channel adjacent the surfaces thereof and supply means being provided to maintain treatment liquid within the channel, the 115 arrangement being such that in the channel the metal foil strip and the treatment liquid can be moved relative to one another at a speed of 0.5—50 m/second.

13. An apparatus as claimed in claim 12, in which the electrodes are themselves constructed as ultrasonic vibrators.

14. An apparatus as claimed in claim 12, in which the electrodes and ultrasonic vibrators face the same metal foil surface 125 in a repeatedly alternating sequence.

15. An apparatus as claimed in claim 12, in which the electrodes and ultrasonic vibrators respectively face opposite metal foil 130 surfaces.

16. An apparatus as claimed in any one of claims 12 to 15, including screens for optionally screening at least partially the electrodes and/or ultrasonic vibrators.
- 5 17. An apparatus as claimed in any one of claims 12 to 16, in which the electrodes are only electrically conducting on the side which faces the metal foil strip.
18. An apparatus as claimed in claim 12, substantially as described herein with reference to Figs. 1 and 2 or Figs. 3 and 4 of the accompanying drawings. 10

ABEL & IMRAY,
Chartered Patent Agents,
Northumberland House,
303—306 High Holborn,
London, WC1V 7LH.

Printed for Her Majesty's Stationery Office by Burgess & Son (Abingdon), Ltd.—1974.
Published at The Patent Office, 25 Southampton Buildings, London, WC2A 1AY,
from which copies may be obtained.

Fig. 1.

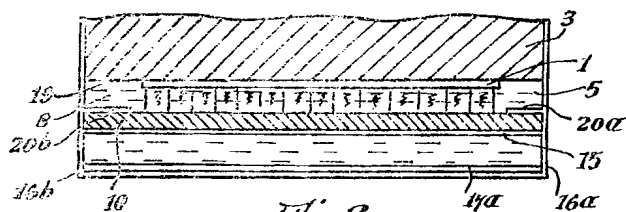
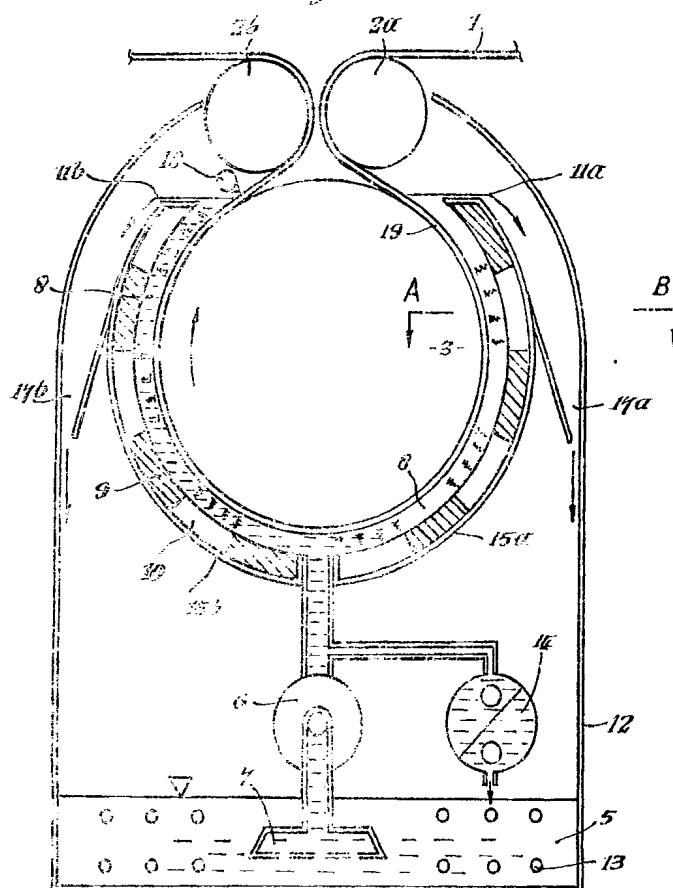


Fig. 2.

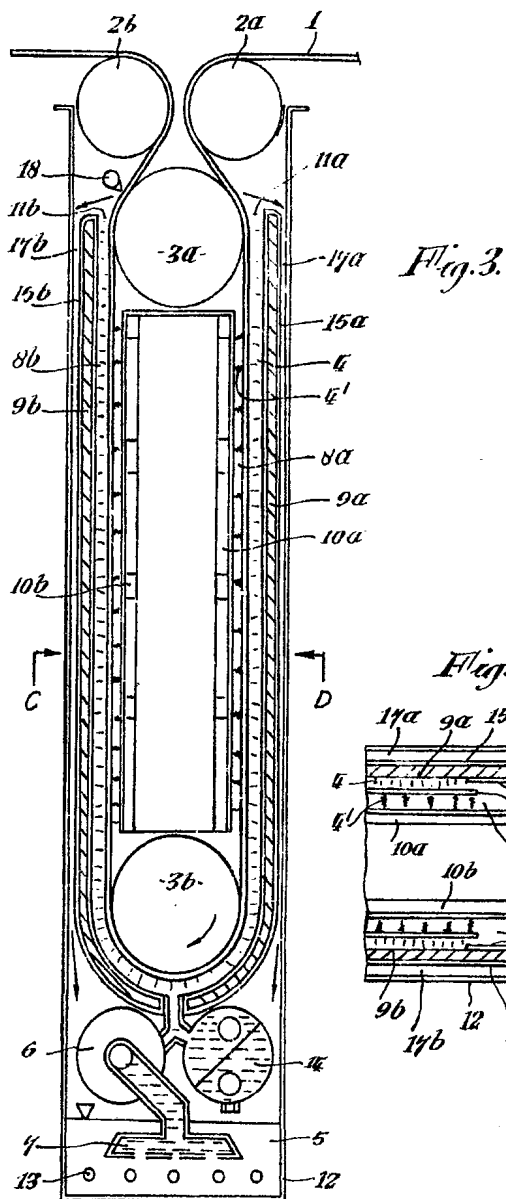


Fig. 3.

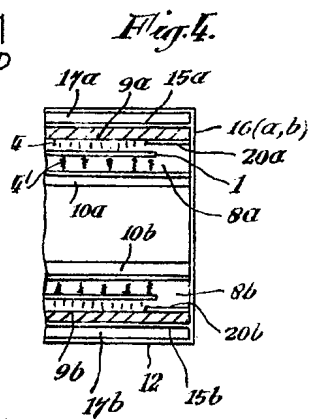


Fig. 4.